

## TENT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
 United States Patent and Trademark  
 Office  
 Box PCT  
 Washington, D.C.20231  
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

|                                                                            |                                                                |
|----------------------------------------------------------------------------|----------------------------------------------------------------|
| Date of mailing (day/month/year)<br>18 May 2000 (18.05.00)                 |                                                                |
| International application No.<br>PCT/US99/20503                            | Applicant's or agent's file reference<br>CM1894M/MH            |
| International filing date (day/month/year)<br>07 September 1999 (07.09.99) | Priority date (day/month/year)<br>07 September 1998 (07.09.98) |
| Applicant<br>D'AGOSTINO, Riccardo et al                                    |                                                                |

1. The designated Office is hereby notified of its election made:

in the demand filed with the International Preliminary Examining Authority on:

16 March 2000 (16.03.00)

in a notice effecting later election filed with the International Bureau on:

\_\_\_\_\_

2. The election  was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

|                                                                                               |                                  |
|-----------------------------------------------------------------------------------------------|----------------------------------|
| The International Bureau of WIPO<br>34, chemin des Colombettes<br>1211 Geneva 20, Switzerland | Authorized officer<br>C. Villet  |
| Facsimile No.: (41-22) 740.14.35                                                              | Telephone No.: (41-22) 338.83.38 |

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

|                                                             |                                                                                                                                                         |                                                                |
|-------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------|
| Applicant's or agent's file reference<br><b>CM1894M/MH</b>  | <b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below. |                                                                |
| International application No.<br><b>PCT/US 99/ 20503</b>    | International filing date (day/month/year)<br><b>07/09/1999</b>                                                                                         | (Earliest) Priority Date (day/month/year)<br><b>07/09/1998</b> |
| Applicant<br><b>THE PROCTER &amp; GAMBLE COMPANY et al.</b> |                                                                                                                                                         |                                                                |

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

contained in the international application in written form.

filed together with the international application in computer readable form.

furnished subsequently to this Authority in written form.

furnished subsequently to this Authority in computer readable form.

the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2.  Certain claims were found unsearchable (See Box I).

3.  Unity of invention is lacking (see Box II).

4. With regard to the title,

the text is approved as submitted by the applicant.

the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

the text is approved as submitted by the applicant.

the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

as suggested by the applicant.

because the applicant failed to suggest a figure.

because this figure better characterizes the invention.

None of the figures.

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C23C16/50 C23C16/30 B05D7/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category <sup>°</sup> | Citation of document, with indication, where appropriate, of the relevant passages                                                             | Relevant to claim No. |
|-----------------------|------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X                     | US 4 632 842 A (KARWOSKI THEODORE ET AL)<br>30 December 1986 (1986-12-30)<br>column 3, line 3 - line 35<br>column 12, line 1 - line 24<br>---  | 1-7                   |
| X                     | EP 0 531 029 A (GEN ELECTRIC)<br>10 March 1993 (1993-03-10)<br>column 4, line 6 - line 31; claims 9-13<br>---                                  | 1,3,5                 |
| A                     | WO 97 42356 A (MASSACHUSETTS INST<br>TECHNOLOGY) 13 November 1997 (1997-11-13)<br>page 9, line 3 -page 15, line 2; claims<br>16,20,24<br>----- | 8-10                  |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

<sup>°</sup> Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

11 January 2000

Date of mailing of the international search report

20/01/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
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Fax: (+31-70) 340-3016

Authorized officer

Patterson, A

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

/US 99/20503

| Patent document cited in search report |   | Publication date | Patent family member(s) |           | Publication date |
|----------------------------------------|---|------------------|-------------------------|-----------|------------------|
| US 4632842                             | A | 30-12-1986       | NONE                    |           |                  |
| EP 0531029                             | A | 10-03-1993       | AU                      | 2128992 A | 04-03-1993       |
|                                        |   |                  | CA                      | 2072384 A | 01-03-1993       |
|                                        |   |                  | CN                      | 1069778 A | 10-03-1993       |
|                                        |   |                  | JP                      | 5230659 A | 07-09-1993       |
|                                        |   |                  | US                      | 5380557 A | 10-01-1995       |
|                                        |   |                  | ZA                      | 9206153 A | 29-05-1993       |
| WO 9742356                             | A | 13-11-1997       | US                      | 5888591 A | 30-03-1999       |
|                                        |   |                  | EP                      | 0920542 A | 09-06-1999       |

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

## (PCT Article 36 and Rule 70)

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                              |                                                                                                     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|
| Applicant's or agent's file reference<br><br>CM1894M/MH                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | <b>FOR FURTHER ACTION</b>                                    | See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) |
| International application No.<br><br>PCT/US99/20503                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | International filing date (day/month/year)<br><br>07/09/1999 | Priority date (day/month/year)<br><br>07/09/1998                                                    |
| International Patent Classification (IPC) or national classification and IPC<br><br>C23C16/50                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                              |                                                                                                     |
| Applicant<br><br>THE PROCTER & GAMBLE COMPANY et al.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                              |                                                                                                     |
| <p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>                                                                                                                                                                                                                                          |                                                              |                                                                                                     |
| <p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> <li>I <input checked="" type="checkbox"/> Basis of the report</li> <li>II <input type="checkbox"/> Priority</li> <li>III <input checked="" type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</li> <li>IV <input type="checkbox"/> Lack of unity of invention</li> <li>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</li> <li>VI <input type="checkbox"/> Certain documents cited</li> <li>VII <input type="checkbox"/> Certain defects in the international application</li> <li>VIII <input checked="" type="checkbox"/> Certain observations on the international application</li> </ul> |                                                              |                                                                                                     |

|                                                                                                                                                                                                                                                                                                                                   |                                                                             |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------|
| Date of submission of the demand<br><br>16/03/2000                                                                                                                                                                                                                                                                                | Date of completion of this report<br><br>15.12.2000                         |
| Name and mailing address of the international preliminary examining authority:<br><br> European Patent Office - P.B. 5818 Patentlaan 2<br>NL-2280 HV Rijswijk - Pays Bas<br>Tel. +31 70 340 - 2040 Tx: 31 651 epo nl<br>Fax: +31 70 340 - 3016 | Authorized officer<br><br>Patterson, A<br><br>Telephone No. +31 70 340 3421 |



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/US99/20503

**I. Basis of the report**

1. This report has been drawn on the basis of (substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.):

**Description, pages:**

1-21 as originally filed

**Claims, No.:**

1-10 as originally filed

**Drawings, sheets:**

1/6-6/6 as originally filed

2. The amendments have resulted in the cancellation of:

the description,      pages:  
 the claims,      Nos.:  
 the drawings,      sheets:

3.  This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

**III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability**

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

the entire international application.  
 claims Nos. 8-10.

because:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/US99/20503

the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

the description, claims or drawings (*indicate particular elements below*) or said claims Nos. 8-10 are so unclear that no meaningful opinion could be formed (*specify*):

**see separate sheet**

the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

no international search report has been established for the said claims Nos. .

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)                    Yes: Claims  
                                    No: Claims 1-7

Inventive step (IS)           Yes: Claims  
                                    No: Claims 1-7

Industrial applicability (IA) Yes: Claims 1-7  
                                    No: Claims

**2. Citations and explanations**

**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**

R It m III

**Non-establishment of opinion with regard to novelty, inventive step and industrial applicability**

Because claims 8-10 are unclear (see item VIII, below) it was not possible to form an opinion with regard to novelty, inventive step and industrial applicability for these claims. No meaningful comparison between the claimed subject-matter and the prior art could be made.

Re Item V

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

The present application does not satisfy the criterion set forth in Article 33(2) PCT because the subject-matter of claims 1-7 is not new in respect of prior art as defined in the regulations (Rule 64(1)-(3) PCT).

Prior art document D1 (US 4 632 842) discloses surface coated substrates having fluorocarbon coatings such that the water contact angle of the surface is greater than 120°, in fact between 140° and 150° in some cases, and the F/C ratio of the coating is 1.7 to 1.8 (see col.3, lines 3-13; col.12, lines 1-24). The subject-matter of claims 1-4 is thus anticipated by D1. Furthermore (see col.3, lines 14-35; examples) the substrate used in D1 corresponds to what is claimed in claims 5-7.

The subject-matter of claims 1,3 and 5 is also known from the second prior art document D2 (EP 0 531 029), which describes a surface treated substrate having a carbon and fluorine based coating and a water contact angle higher than 120°. Such a coating is considered to constitute a fluorocarbon coating. The coating is deposited on substrates such as metals and ceramics (see col. 4, lines 6-31).

As a consequence of not being new, claims 1-7 cannot involve an inventive step either.

**R Item VIII**

**C certain observations on the international application**

The application does not meet the requirements of Article 6 PCT, because claims 4,6 and 8-10 are not clear.

With respect to claim 6, it is observed that examination of a coated substrate cannot reveal whether or not the porosity of the substrate has been affected by the application of the coating. The act of coating a substrate without affecting its porosity is purely a process feature. Moreover the wording of claim 6, and also claim 4, subsequent to "preferably" has no limiting effect whatsoever.

Claims 8-10 contain exclusively "product-by-process" features. Since it is unclear how, if at all, the characteristics of the finished product are affected by the various steps in its manufacture, it is impossible to ascertain how the subject-matter of these claims differs from that of any one of the claims upon which they depend. By the same token, the skilled person cannot tell whether the process steps mentioned in the claims produces a difference between the claimed subject-matter and what is disclosed in the prior art.

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |  |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|
| (51) International Patent Classification <sup>7</sup> :<br><br>C23C 16/50, 16/30, B05D 7/24                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |  | A1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | (11) International Publication Number: <b>WO 00/14296</b><br><br>(43) International Publication Date: 16 March 2000 (16.03.00) |
| (21) International Application Number: PCT/US99/20503                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  | (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).<br><br><i>SAME</i>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                |
| (22) International Filing Date: 7 September 1999 (07.09.99)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |  | (81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KR (Utility model), KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).<br><br><b>Published</b><br><i>With international search report.</i><br><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |                                                                                                                                |
| (30) Priority Data:<br>98116894.1 7 September 1998 (07.09.98) EP<br><br><i>SAME</i>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |  | (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).<br><br><i>SAME</i>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                |
| (72) Inventors; and<br><br>(75) Inventors/Applicants (for US only): D'AGOSTINO, Riccardo [IT/IT]; Via Orabona, 4, I-70126 Bari (IT). CORZANI, Italo [IT/IT]; Via Fontevecchia, 40, I-66100 Chieti (IT). DATTA, Saswati [US/US]; 11636 Plumhill Lane, Cincinnati, OH 45249 (US). FAVIA, Pietro [IT/IT]; Via Orabona, 4, I-70126 Bari (IT). FRANCE, Paul, Amaat, Raymond, Gerard [BE/US]; 8375 Todd Creek Circle, West Chester, OH 45069 (US). LAMENDOLA, Ritalba [IT/IT]; Via Orbona, 4, I-70126 Bari (IT). PALUMBO, Gianfranco [DE/DE]; Georgenfeld 7, D-61348 Bad Homburg (DE). RADOMYSELSKIY, Arseniy Valerevich [UA/US]; 1031 Delta Avenue 31, Cincinnati, OH 45208 (US). |  |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                |

(54) Title: SUPER HYDROPHOBIC COATED SUBSTRATES

## (57) Abstract

This invention deals with a continuous, fluorocarbon thin film with super hydrophobic surface characteristics, i.e. characterized by static water contact angle values higher than about 120°, preferably higher than 130°, more preferably higher than 150°, which is tightly bound to the substrate.

***FOR THE PURPOSES OF INFORMATION ONLY***

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

|    |                          |    |                                       |    |                                           |    |                          |
|----|--------------------------|----|---------------------------------------|----|-------------------------------------------|----|--------------------------|
| AL | Albania                  | ES | Spain                                 | LS | Lesotho                                   | SI | Slovenia                 |
| AM | Armenia                  | FI | Finland                               | LT | Lithuania                                 | SK | Slovakia                 |
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| BJ | Benin                    | IE | Ireland                               | MR | Mauritania                                | UA | Ukraine                  |
| BR | Brazil                   | IL | Israel                                | MW | Malawi                                    | UG | Uganda                   |
| BY | Belarus                  | IS | Iceland                               | MX | Mexico                                    | US | United States of America |
| CA | Canada                   | IT | Italy                                 | NE | Niger                                     | UZ | Uzbekistan               |
| CF | Central African Republic | JP | Japan                                 | NL | Netherlands                               | VN | Viet Nam                 |
| CG | Congo                    | KE | Kenya                                 | NO | Norway                                    | YU | Yugoslavia               |
| CH | Switzerland              | KG | Kyrgyzstan                            | NZ | New Zealand                               | ZW | Zimbabwe                 |
| CI | Côte d'Ivoire            | KP | Democratic People's Republic of Korea | PL | Poland                                    |    |                          |
| CM | Cameroon                 | KR | Republic of Korea                     | PT | Portugal                                  |    |                          |
| CN | China                    | KZ | Kazakhstan                            | RO | Romania                                   |    |                          |
| CU | Cuba                     | LC | Saint Lucia                           | RU | Russian Federation                        |    |                          |
| CZ | Czech Republic           | LJ | Liechtenstein                         | SD | Sudan                                     |    |                          |
| DE | Germany                  | LK | Sri Lanka                             | SE | Sweden                                    |    |                          |
| DK | Denmark                  | LR | Liberia                               | SG | Singapore                                 |    |                          |

## INTERNATIONAL SEARCH REPORT

Final Application No

PCT/US 99/20503

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C16/50 C23C16/30 B05D7/24

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages                                                             | Relevant to claim No. |
|----------|------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X        | US 4 632 842 A (KARWOSKI THEODORE ET AL)<br>30 December 1986 (1986-12-30)<br>column 3, line 3 - line 35<br>column 12, line 1 - line 24<br>---  | 1-7                   |
| X        | EP 0 531 029 A (GEN ELECTRIC)<br>10 March 1993 (1993-03-10)<br>column 4, line 6 - line 31; claims 9-13<br>---                                  | 1,3,5                 |
| A        | WO 97 42356 A (MASSACHUSETTS INST<br>TECHNOLOGY) 13 November 1997 (1997-11-13)<br>page 9, line 3 -page 15, line 2; claims<br>16,20,24<br>----- | 8-10                  |

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

11 January 2000

Date of mailing of the international search report

20/01/2000

Name and mailing address of the ISA

European Patent Office, P.O. Box 5818 Patentlaan 2  
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Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Patterson, A

## INTERNATIONAL SEARCH REPORT

Information on patent family members

National Application No.

PCT/US 99/20503

| Patent document cited in search report |   | Publication date | Patent family member(s) |           | Publication date |
|----------------------------------------|---|------------------|-------------------------|-----------|------------------|
| US 4632842                             | A | 30-12-1986       | NONE                    |           |                  |
| EP 0531029                             | A | 10-03-1993       | AU                      | 2128992 A | 04-03-1993       |
|                                        |   |                  | CA                      | 2072384 A | 01-03-1993       |
|                                        |   |                  | CN                      | 1069778 A | 10-03-1993       |
|                                        |   |                  | JP                      | 5230659 A | 07-09-1993       |
|                                        |   |                  | US                      | 5380557 A | 10-01-1995       |
|                                        |   |                  | ZA                      | 9206153 A | 29-05-1993       |
| WO 9742356                             | A | 13-11-1997       | US                      | 5888591 A | 30-03-1999       |
|                                        |   |                  | EP                      | 0920542 A | 09-06-1999       |



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: SUPER HYDROPHOBIC COATED SUBSTRATES

## (57) Abstract

This invention deals with a continuous, fluorocarbon thin film with super hydrophobic surface characteristics, i.e. characterized by static water contact angle values higher than about 120°, preferably higher than 130°, more preferably higher than 150°, which is tightly bound to the substrate.

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## Super hydrophobic coated substrates

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### Field of the invention

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The present invention relates to super hydrophobic coated substrates having a static water contact angle of more than 120°.

### Background of the invention

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For instance, U.S. Pat. No. 3,498,527 teaches that paper board containers for liquids can be waterproofed by application of a waterproofing coating such as wax or polyethylene, and a similar method is shown in U.S. Pat. No. 2,708,645 for waterproofing paper drinking cups and in U.S. Pat. No. 3,212,697 for paper grocery sacks. In U.S. Pat. No. 3,597,313, temporary wet strength is imparted to paper by coating it with a polymeric alcohol-polymeric aldehyde reaction product.

Coating processes, by themselves, have been used to produce disposable articles of sanitary clothing. In U.S. Pat. No. 3,078,849, a disposable sanitary napkin is disclosed which consists of an adsorbent layer having a liquid-repellent backing of polyvinyl alcohol or similar material capable of initially repelling water but eventually solubilizing. The degree of water-repellency, therefore the lifetime of the napkin, is controlled by varying the thickness of the backing. Because the

necessary life of the napkin cannot be predicted by manufacturer or user, the backing must be sufficiently thick to take account of all normal contingencies. U.S. Pat. No. 3,542,028 is directed to a flushable sanitary napkin consisting of a cellulosic sheet treated with a fluoropolymer coating. U.S. Pat. No. 3,559,650 5 teaches the preparation of a sanitary napkin having two flush-disposable sides separated by a waterproof film too thin to support itself once both faces of the napkin have disintegrated upon disposal.

Analogous to the process of coating a surface with a waterproofing substance is 10 the concept of reacting a surface with another material so as to form a reaction product on the surface which has water-repellent properties. For example, U.S. Pat. Nos. 2,130,212 and 3,137,540 teach that materials such as polymeric alcohols may be reacted with other materials to increase their water-repellent properties. The latter patent teaches treating polyvinyl alcohol articles with an 15 aqueous emulsion of an aldehyde to impart water-repellency thereto. U.S. Pat. No. 3,626,943 teaches that disposable diapers can be made from polyvinyl alcohol and waterproofed on one side by reaction with formaldehyde. These reaction-type coating processes suffer from drawbacks. They are carried out in the aqueous phase which is complicated and requires relatively large quantities 20 of reagents. Most of the processes which employ some form of in situ chemical reaction to produce a water-repellent surface are carried out in the liquid phase, some vapor phase treatments are taught by U.S. Pat. Nos. 2,306,222; 2,961,388; and 3,017,290.

25 A known method of water and oil repellent finishing of textiles, described in USSR Patent 1,158,634, includes plasma treatment in a glow discharge in an atmosphere of inorganic gases, followed by treatment with a fluorine containing acrylic monomer in gas phase. Another prior method of achieving film plasma polymerization, described in U.S. Pat. No. 4,188,426, includes treatment in a 30 glow discharge of per-fluoro-cyclo-butane or hexafluoroethane to reduce the friction coefficient and to improve the surface hydrophobia of organic and

inorganic substrates (e.g. polyethylene films, metals). However these disclosures do not achieve a level of water repellency as the present invention.

Plasma-deposited fluorocarbon coatings are often cited in the literature as 5 "teflon-like coatings" because their  $CF_x$  ( $0 < x \leq 2$ ) composition and surface energy can be made very close to that of polytetrafluoroethylene (PTFE,-( $CF_2-CF_2-$ )<sub>n</sub>), known on the market as Teflon®.

Plasma coating processes of metals, polymers, and other substrates, with fluorocarbon films are known in the art. As an example, it is known from USP 10 4 869 922 and from other sources, that deposition from continuous (i.e. non modulated) radiofrequency (RF) glow discharges fed with fluorocarbons provides films, layers, tapes, plates, and differently shaped articles made of plastics, metals or other materials, with a thin fluorocarbon coating, with no other material interposed between the coating itself and the substrate. Such coatings are claimed 15 to have very good adherence to the items processed, to be void-free, to be uniform or not porous, and to show controlled wettability characteristics, which depend on their surface chemical composition. The non modulated, continuous plasma process of the above mentioned patent leads to coatings characterized 20 by static water contact angle (WCA) values lower than 120°.

Glow discharges treatments are also considered in US-A-5 462 781 for improving the bondability of an implantable polymer medical device or for changing the wettability of a polymer fabric. Several of the references discussed in this patent 25 confirm non modulated, continuous plasma treatments as a means for varying the inherent WCA of a surface.

US-A-5 034 265 discloses a non modulated, continuous plasma treatment for improving the biocompatibility of vascular grafts with a  $CF_x$  fluorocarbon coating 30 deposited at the inside wall of the grafts in a proper plasma reactor fed with tetrafluoroethylene ( $C_2F_4$ , TFE) at 0.2 Torr. In the preferred embodiment of the

invention no other materials are interposed between the substrate and the coating.

U.S. Pat No 5,328,576 discloses a method for imparting water and oil repellent 5 surface properties to fabrics or paper that includes pretreatment in a low pressure oxygen plasma in the presence of water vapor followed by plasma polymerization of methane in a high frequency glow discharge carried out in the same treatment chamber. This method doesn't deliver durable, permanent coatings with a WCA higher than about 120°.

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U.S. Pat. No. 5,262,208 discloses an gas plasma treatment for archival preservation of paper manuscripts by a thin film protective polymer film. The treatment time is ranging from 30-3600 seconds. Other methods have been used to obtain thin coatings on the web materials with short treatment periods.

15 Providing surface treatment is disclosed in US Patent No. 4,842,893 and 4,954,371 which describe a process for high speed coating of substrates with a complete and uniformly adhering layer and using electron beam radiation curing of the vapor deposited monomers for multilayer capacitors. U.S. Pat. No. 4,842,893 discloses high speed coating process including flash vaporization 20 system and electron beam curing. Both of these electron beam disclosures are incorporated herein by reference. Other uses of electron beam coatings in the electronic industry field have been reported by Westinghouse science & technology center USA (Adv. Mat. Newsletter Volume 13, No 9, 1991 page 4).

25

### Summary of the invention

Specifically, the present invention, having the features mentioned in the annexed claims, relates to substrates coated with a thin, well adherent, nonporous, fluorocarbon coating with super hydrophobic properties, i.e. characterized by static 30 water contact angle (WCA) values, measured on a smooth and plane surface, higher than about 120°, preferably higher than 130°, more preferably higher than 150°. Substrates treated with this method have their hydrophobicity markedly

improved, e.g. can be made effectively waterproof while maintaining their previous characteristics such as permeability to gases and vapors. The increased hydrophobicity results also in additional benefits such as prevention of build-up of soiling (e.g. on hard surfaces such as glass, ceramics, metals and other surfaces exposed to dirt), prevention of lumping of powders or granules, aiding in complete emptying of containers which contain hydrophilic materials such as liquid detergent or shampoo bottles or beverage containers or liquid tanks or flowable particle tanks e.g. flour tanks, prevention of contamination and build-up on tooth-brushes and bristles. If the substrates are polymeric, they can be useful e.g. in making breathable products with improved resistance to leakage of body fluids.

The present invention deals with treated polymeric or non polymeric articles whose surface is made super hydrophobic, i.e. characterized by static water contact angle (WCA) values higher than about 120°, preferably higher than 130°, more preferably higher than 150°.

The substrates of interest for the present invention may include a wide range of materials in form of webs, tapes, films, powders, granules, particles, woven and non-woven layers; substrates can be porous or non-porous, molded or shaped, rigid or flexible, made of polymers, textiles, papers, cellulose derivatives, biodegradable materials, metals, ceramics, semiconductors, and other inorganic or organic materials. Preferably, the substrate is formed into a desired shape or configuration, depending on its intended use, before being subjected to the treatment object of this invention.

25

When organic synthetic resins are chosen, such substrate materials could be fabricated from polyethylene, polyacrylics, polypropylene, polyvinyl chloride, polyamides, polystyrene, polyurethanes, polyfluorocarbons, polyesters, silicone rubber, hydrocarbon rubbers, polycarbonates and other synthetic polymers.

30

The articles are preferably subjected to a modulated glow discharge plasma treatment performed with a fluorocarbon gas or vapor compound fed in a prop-

erly configured reactor vessel where the substrates are positioned. The plasma process deposits a continuous, fluorocarbon thin film with super hydrophobic surface characteristics, tightly bound to the substrate.

- 5 Alternatively a more conventional thin film coating process followed by high energy surface curing can be used. This is the method of using a high speed vacuum coating process for producing durable and thin water-repellent coatings on a substrate. It uses e.g. a movable support such as rotating drum in a vacuum chamber. The surface of the support is maintained at a temperature sufficient to
- 10 permit condensation of a vaporized material deposited in the chamber. The material is a curable monomer with a relatively low molecular weight. The monomer vapor is created using a flash vaporizer. The desired amount of curable monomer is metered to a heated flash vaporizer system where the material is vaporized. It is then transported e.g. by its inherent pressure, to the
- 15 substrate resting on the rotating drum and condensed on the surface of the substrate. According to the method the substrate is then transported to a curing means such as an energy source which emits an electron beam, UV-light radiation or exposure to an electro magnetic field. Alternative the curable monomer can also be transferred into radicals by passing through a plasma zone
- 20 (zone of high voltage discharge). The curing of the monomer by the curing means then provides a coating on the substrate surface which has a static water contact angle of more than 95°.

The method for delivering the curable monomer to the substrate for minimizing the amount of monomers can use an ultrasonic atomizer producing micro droplets of curable monomer. They are released into a vaporization tube heated by band heaters. The atomized droplets impinge on the inner wall of the vaporization tube and are instantaneously vaporized, i.e., flash vaporized. This reduces the opportunity for polymerization prior to being deposited on the

25 substrate.

30

In one aspect of the present invention, the substrate can be one side water-repellent and capable of absorbing and storing fluids from the other side, or alternatively be repellent on both sides.

5 "Plasma," as used herein, is used in the sense of "low-temperature plasma" or "cold plasma" produced by igniting a glow discharge in a low pressure gas through a power supply. Glow discharges contain a variety of species chemically active and energetic enough to cause chemical reactions with surfaces exposed, i.e. covalent bonding to a suitable substrate material. Cold plasmas, or glow dis-

10 charges, are generally produced with high frequency (from KHz to MHz and GHz) power supply (HF plasmas). Electrons, positive and negative ions, atoms, excited molecules, free radicals, and photons of various energies are formed in a cold plasma.

15 "Modulated plasma" means a non continuous plasma, HF plasma, i.e. a glow discharge whose driving power is pulsed between a maximum value and zero (ON/OFF pulse) or a fraction of it, at a certain frequency, with a proper pulse generator connected to the main power supply. In the case of ON/OFF pulsed systems, the time ON and time OFF values are among the experimental pa-

20 rameters of the process. Superimposing a triggering ON/OFF pulse to the main high frequency field which generally drives a glow discharge, alternates short continuous discharges with plasma OFF time intervals where active species still exists in the gas phase, but the effects of ions and electrons are strongly reduced. This alternating exposure to two different processes leads to unique sur-

25 face modifications of substrates, which are very different from those of continuous plasma process, as it will be shown.

"Plasma deposition" or "plasma polymerization" is the plasma process that leads to the formation of thin (0.01 - 2  $\mu$ m), partly crosslinked, void-free, continuous

30 coatings well adherent to substrates. The molecules of the gas phase are fragmented by energetic electrons, which are able to break chemical bonds; this process leads to radicals and other chemical species which are able to deposit at

surfaces inside the vacuum chamber and form a thin, uniform film. The action of the plasma may also affect the surface of a polymer substrate in the early deposition time; energetic species may break bonds in the substrate with possible evolution of gas products, such as hydrogen, and formation of free radical sites  
5 which contribute to form covalent bonds between the growing film and the substrate.

Substrate to be treated are subjected to modulated plasma gas discharge in the presence of at least one fluorocarbon gas or vapor. Specifically, fluorocarbon  
10 gases or vapors such as tetrafluoroethylene (TFE,  $C_2F_4$ ), hexafluoropropene (HFP,  $C_3F_6$ ), perfluoro-(2-trifluoromethyl-)pentene, perfluoro-(2-methylpent-2-ene) or its trimer may be used, TFE being the presently preferred choice. The plasma deposition process is preferably performed by positioning the substrate in a properly arranged plasma reactor, connecting the reactor to a source of a fluorocarbon gas or vapor, regulating flow and pressure of the gas inside the reactor, and sustaining a glow discharge in the reactor with a high frequency electric field  
15 in a pulsed (modulated) mode by means of a suitable pulsed power supply. The parameters which define the glow discharge treatment includes the feed gas or vapor, its flow rate, its pressure, the position of the substrate inside the reactor,  
20 the design of the reactor, the exciting frequency of the power supply, the input power, the time ON and the time OFF of the pulsing system. Substrates, as those listed in the abstract, may be positioned in the "glow" region of the discharge, i.e. directly exposed to the plasma, or in the "afterglow" region, i.e. downstream respect to the visible glow. The two positions generally result in  
25 coatings with different composition and properties; treating the substrates with modulated glow discharge results also in different coatings respect to continuous treatments.

It has been found that it is possible to deposit thin fluorocarbon films with super  
30 hydrophobic characteristics, i.e. showing a surprisingly high WCA value, even up to about 165°. The present invention thus provides substrates of the type mentioned above, with fluorocarbon films characterized by a WCA value higher than

120°, preferably higher than 130°, more preferably higher than 150°.

According to the present invention, fluorocarbon coatings with F/C ratio from about 1.50 to about 2.00 have been deposited, characterized by WCA values 5 higher than about 120°, such as between about 155° and about 165°. The coatings have been deposited at the surface of different polymer and non polymer substrates such as polyethylene (PE), polypropylene (PP) polyethyleneterephthalate (PET), and paper in form of films and fabrics, glass and silicon, among many. It should be noted that the F/C ratio could be theoretically up to 3, if the 10 coating would be formed only by a mono-molecular layer of  $CF_3$  groups. But the formation of intermolecular cross-links and the formation of claims (containing  $CF_2$  fragments) which are grafted onto the surface lowers the above theoretical value so that the obtained coatings, notwithstanding the fact that they contain many  $CF_3$  groups, have a global F/C ratio in the range of about 1.50 to about 15 2.00.

The thickness of the coatings depends on the duration of the plasma process at different conditions, and can be kept between 0.01 and 2  $\mu$ m. It has been found that the nature of the substrate materials does not influence neither the chemical 20 composition nor the thickness of the coatings. Coatings with WCA values up to about 165° (e.g.  $165^\circ \pm 5^\circ$ ) were obtained.

#### Brief description of the drawings

25 In the following detailed description the invention will be described, purely by way of example, with reference to the enclosed figures of drawing, wherein:

- Figure 1 compares a conventional "continuous" RF glow discharge with an ON/OFF "modulated" RF glow discharge;
- Figure 2 portrays a typical scheme of a plasma reactor adapted for use 30 within the context of the invention;
- Figure 3 shows a C1s ESCA signal of an uncoated polyethylene substrate wherein the signal is due only to C-H, C-C bonds of the substrate;

- Figure 4 shows a C1s ESCA signal of a PE substrate coated with a fluorocarbon coating deposited as described in example 1 (glow position, continuous mode), with WCA of  $100 \pm 5^\circ$ ; the signal is composed by components due to CF3, CF2, CF and CCF bonds of the fluorocarbon coating, and to C-H, C-C bonds due to surface contamination;

- Figure 5 shows a C1s ESCA signal of a PE substrate coated with a fluorocarbon coating deposited as described in example 1 (afterglow position, continuous mode), with WCA of  $120 \pm 5^\circ$ ; the signal is composed by components due to CF3, CF2, CF and CCF bonds of the fluorocarbon coating, and to C-H, C-C bonds due to surface contamination; and

- Figure 6 shows a C1s ESCA signal of a PE substrate coated with a fluorocarbon coating deposited as described in example 1 (glow position, modulated mode), with WCA of  $165 \pm 5^\circ$ ; the signal is composed by components due to CF3, CF2, CF and CCF bonds of the fluorocarbon coating, and to C-H, C-C bonds due to surface contamination.

#### Detailed description of the invention

Figure 1 compares a conventional "continuous" plasma (figure 1a) with the modulated process of the invention, (figure 1b) showing pulsed alternating plasma ON with plasma OFF (i.e. no plasma) times. The two processes are schematized by referring to their driving signals.

The reactor 1 schematically shown in figure 2 was utilized not exclusively for developing the deposition method object of the present invention. The reactor vacuum chamber 1 is made of Pyrex glass, is provided with an external RF powered electrode 2 and an internal grounded electrode 3. The external electrode is connected to a power supply 4 (typically a radiofrequency generator operating at e.g. 13.56 MHz) through a matching network and an ON/OFF pulse generator 5. The substrates can be treated in the "glow" region of the reactor, onto the grounded electrode 3, as well as in its "afterglow" position i.e. at an afterglow substrate holder 6. The gas/vapor is fed through a proper mass flowmeter through a

gas/vapor feeding manifold 7, and its pressure, measured at the pump out exit 8 of the reactor, kept at a certain constant value with a manual valve on the vacuum connection between the reactor and its pumping unit. Even though the arrangement shown in the drawing represents a presently preferred choice, those skilled in the art will immediately recognize that pulsed energization of the plasma reactor can be achieved by different means such as direct energization by means of pulsed RF generators commonly used in radar and telecommunication techniques.

10 Preferably, the deposition process is performed with an RF (13.56 MHz) generator. The RF power delivered to the external electrode of the reactor is kept in the 1-500 Watts range for a power density of 0.02-10 Watt/cm<sup>2</sup>. The reactor is fed with a fluorocarbon compound at a 1-100 sccm flow rate and is kept at a constant pressure of 50-1000 mTorr during the process. Preferably, the glow discharges are modulated through the pulse generator, preferably at 1-500 ms time 15 ON and 1-1000 ms time OFF values, with respective values of about 10 ms and about 190 ms being the most preferred choice at present. The deposition process may range from a few seconds to many hours; during this time a uniform fluorocarbon coating is deposited on the substrates positioned in the glow as well 20 as on those in the afterglow region. The deposition rate, a typical one being in the 20 - 400 Å/min range, was measured by weighing (weight/time) the substrates before and after the discharge, or by measuring the thickness of the coatings (thickness/time) with an Alpha Step profilometer. The deposition rate and the chemical composition of the coating depend on the experimental conditions (pressure, power, substrate position time ON, time OFF, gas feed and flow 25 rate) of the discharge.

The coatings obtained are uniform over the entire surface of the substrate; when deposited on flat (i.e. plane), smooth substrates, their hydrophobic character has 30 been estimated through their static WCA value, as measured with a WCA goniometer. The measurement is done on a flat, i.e. plane, and smooth surface of a substrate after coating. The term smooth as used herein for water contact angle

measurements refers to a roughness of no more than 5 microns in accordance with standard roughness measurements on continuous surfaces. WCA values in the range about 120° to about 165°, corresponding to a critical surface tension lower than that of PTFE (18 dynes/cm) have been measured for fluorocarbon 5 CF<sub>x</sub> coatings, when x ranges between about 1.50 and about 2.00. The chemical composition of coatings is preferably determined by Electron Spectroscopy for Chemical Analysis (ESCA) within the sampling depth of the technique (about 100 Å). The adherence of the coating to the substrate is very good.

10 The following examples are given for the purpose of still better illustrating the inventive concept of the present invention, and for highlighting the advantages of using modulated over continuous treatments.

#### EXAMPLE 1

15 Three sets of substrates of silicon, PE and PP, of areas in the range of 2-10 cm<sup>2</sup> per substrate, were positioned onto the grounded electrode 3 of the reactor schematized in Figure 2. A similar set of substrates was positioned in the afterglow position at 6. C<sub>2</sub>F<sub>4</sub> was set to feed continuously the reactor at 6 sccm, and 20 the pressure set at 300 mTorr. The RF generator was connected to the reactor and allowed to sustain the discharge with 50 Watt of input power for 90 min, then switched off.

25 Another glow discharge was subsequently run with a similar set of substrates positioned in the glow position and no substrates in the afterglow position, under the same conditions described above except for the fact that modulation was effected at 10 ms time ON and 190 ms time OFF through the pulse generator.

At the end of the two discharges the substrates were extracted from the reactor 30 and their WCA measured. The WCA values shown in Table 1 were found, which are compared to the WCA values of the unprocessed substrates. A deposition rate of 30 ± 5 Å/min was measured for the coatings deposited in the modulated

mode.

Other substrates, treated in the two modes, were analysed with the ESCA technique. Their surface composition resulted to be entirely composed by carbon and fluoride (fluorine as element), according to the results shown in Tables 2a-c. No other elements were detected (e.g. Si for silicon substrates), which means that the coatings are continuous. The C1s spectrum of the uncoated PE substrate is shown in Figure 3, while the C1s spectra of PE samples coated as described above are shown in Figures 4, 5 and 6, respectively.

10

Table 1

| SUBSTRATE                                        | Si        | PE        | PP        |
|--------------------------------------------------|-----------|-----------|-----------|
| WCA unprocessed                                  | 15° ± 3°  | 95° ± 3°  | 85° ± 3°  |
| WCA continuous discharge<br>(glow position)      | 100° ± 5° | 100° ± 5° | 100° ± 5° |
| WCA continuous discharge<br>(afterglow position) | 120° ± 5° | 120° ± 5° | 120° ± 5° |
| WCA modulated discharge<br>(glow position)       | 165° ± 5° | 165° ± 5° | 165° ± 5° |

Table 2a

15 ESCA results for the continuous discharge (glow position) of Example 1

| COATED SUBSTRATE  | Si   | PE   | PP   |
|-------------------|------|------|------|
| carbon atomic %   | 43.3 | 42.4 | 42.9 |
| fluorine atomic % | 56.7 | 57.6 | 57.1 |
| F/C ratio         | 1.31 | 1.36 | 1.33 |

Table 2b

ESCA results for the continuous discharge (afterglow position) of Example 1

| COATED SUBSTRATE  | Si   | PE   | PP   |
|-------------------|------|------|------|
| carbon atomic %   | 34.4 | 33.8 | 34.1 |
| fluorine atomic % | 65.6 | 66.2 | 65.9 |
| F/C ratio         | 1.91 | 1.96 | 1.93 |

Table 2c

ESCA results for the modulated discharge (glow position) of Example 1

5

| COATED SUBSTRATE  | Si   | PE   | PP   |
|-------------------|------|------|------|
| carbon atomic %   | 36.4 | 36.2 | 36.7 |
| fluorine atomic % | 63.6 | 63.8 | 63.3 |
| F/C ratio         | 1.75 | 1.76 | 1.72 |

EXAMPLE 2

Three sets of substrates of glass, silicon and PE, of areas in the range of 2-10 cm<sup>2</sup> per substrate, were positioned onto the grounded electrode 3 of the reactor schematized in Figure 2. A similar set of substrates was positioned in the afterglow position. C<sub>3</sub>F<sub>6</sub> was set to feed continuously the reactor at 5 sccm, and the pressure set at 300 mTorr. The RF generator was connected to the reactor and allowed to sustain the discharge with 50 Watt of input power for 60 min, then switched off.

Another glow discharge was subsequently run with a similar set of substrates positioned in the glow position and no substrates in the afterglow, under the same conditions described above except for the fact that modulation was effected at 10 ms time ON and 90 ms time OFF through the pulse generator.

At the end of the two discharges the substrates were extracted from the reactor and their WCA measured. The WCA values shown in Table 3 were found, which

are compared to the WCA values of the unprocessed substrates. A deposition rate of  $70 \pm 5 \text{ \AA/min}$  was measured for the coatings deposited in the modulated mode.

5 Other substrates, treated in the two modes, were analysed with the ESCA technique; their surface composition resulted to be entirely composed by carbon and fluoride (fluorine as element), according to the results shown in Tables 4a-c. Also for this case, since no other elements were detected (e.g. Si for silicon and glass substrates), the coatings were assumed to be continuous.

10

Table 3

| SUBSTRATE                                        | glass                   | Si                      | PE                      |
|--------------------------------------------------|-------------------------|-------------------------|-------------------------|
| WCA unprocessed                                  | $35^\circ \pm 3^\circ$  | $15^\circ \pm 3^\circ$  | $95^\circ \pm 3^\circ$  |
| WCA continuous discharge<br>(glow position)      | $105^\circ \pm 5^\circ$ | $105^\circ \pm 5^\circ$ | $105^\circ \pm 5^\circ$ |
| WCA continuous discharge<br>(afterglow position) | $120^\circ \pm 5^\circ$ | $120^\circ \pm 5^\circ$ | $120^\circ \pm 5^\circ$ |
| WCA modulated discharge<br>(glow position)       | $120^\circ \pm 5^\circ$ | $120^\circ \pm 5^\circ$ | $120^\circ \pm 5^\circ$ |

Table 4 a

ESCA results for the continuous discharge (glow position) of Example 2

| COATED SUBSTRATE  | glass | Si   | PE   |
|-------------------|-------|------|------|
| carbon atomic %   | 42.7  | 42.1 | 41.5 |
| fluorine atomic % | 57.3  | 57.9 | 58.5 |
| F/C ratio         | 1.34  | 1.37 | 1.41 |

15

Table 4 b

ESCA results for the continuous discharge (afterglow position) of Example 2

| COATED SUBSTRATE | glass | Si | PE |
|------------------|-------|----|----|
|                  |       |    |    |

|                   |      |      |      |
|-------------------|------|------|------|
| carbon atomic %   | 37.1 | 38.3 | 38.1 |
| fluorine atomic % | 62.9 | 61.7 | 61.9 |
| F/C ratio         | 1.69 | 1.61 | 1.62 |

Table 4 c

ESCA results for the modulated discharge (glow position) of Example 2

| COATED SUBSTRATE  | glass | Si   | PE   |
|-------------------|-------|------|------|
| carbon atomic %   | 38.1  | 39.9 | 39.2 |
| fluorine atomic % | 61.9  | 60.1 | 60.8 |
| F/C ratio         | 1.62  | 1.51 | 1.55 |

5

EXAMPLE 3

Three set of substrates of polished silicon, polyethyleneterephthalate (PET), and 3 mm thick FAM (Functional Absorbent Material), an hydrophilic absorbent material 10 made according to the teachings of USP 5 260 345, of areas in the range of 2-10 cm<sup>2</sup> per substrate, were positioned onto the grounded electrode 3 of the reactor schematized in Figure 1. C<sub>2</sub>F<sub>4</sub> was set to feed continuously the reactor at 5 sccm, and the pressure set at 400 mTorr. The RF generator was connected to the reactor and allowed to sustain the discharge for 20 min in the modulated mode (10 15 ms time ON; 190 ms time OFF) with 75 Watt of input power. At the end of the discharge the substrates were extracted from the reactor, and their WCA measured. The values shown in Table 5 were found, which are compared to the WCA values of the unprocessed substrates. A deposition rate of 300 ± 10 Å/min was measured.

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Other substrates were ESCA analysed; their surface composition resulted to be entirely composed by carbon and fluoride (fluorine as element), according to the results shown in Table 6. No other elements have been detected (e.g. Si for silicon substrates, and O for PET substrates ), thus the coatings can be assumed to

be continuous.

The coated FAM substrate was cut along its thickness, and the freshly cut surface, which was not directly exposed to the discharge, analysed by WCA and 5 ESCA measurements. The data shown in Table 7 demonstrate that the thick FAM sample was treated not only on the surface exposed to the glow, but also inside its bulk, which demonstrates that the plasma treatment is able to penetrate through porous substrates.

10 Table 5

| SUBSTRATE                               | PET                     | Si                      | FAM                                                    |
|-----------------------------------------|-------------------------|-------------------------|--------------------------------------------------------|
| WCA unprocessed                         | $75^\circ \pm 3^\circ$  | $15^\circ \pm 3^\circ$  | WCA unmeasurable, the drop is adsorbed by the material |
| WCA modulated discharge (glow position) | $155^\circ \pm 5^\circ$ | $155^\circ \pm 5^\circ$ | $155^\circ \pm 10^\circ$                               |

15

Table 6

ESCA results for the modulated discharge (glow position) of Example 3

| COATED SUBSTRATE  | PET  | Si   | FAM  |
|-------------------|------|------|------|
| carbon atomic %   | 34.8 | 35.6 | 34.0 |
| fluorine atomic % | 65.2 | 64.4 | 66.0 |
| F/C ratio         | 1.87 | 1.81 | 1.94 |

20

Table 7

ESCA results for the treated FAM sample of Example 3 cut just after the treatment

5

| SUBSTRATE                | bulk FAM, cut after the treatment                                                                                                                                         |
|--------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| WCA(modulated discharge) | the drop of water is not absorbed<br><br>the material is evidently much more hydrophobic respect to the untreated one<br><br>WCA is unmeasurable due to surface roughness |
| carbon atomic %          | 38.5                                                                                                                                                                      |
| fluorine atomic %        | 61.5                                                                                                                                                                      |
| F/C ratio                | 1.60                                                                                                                                                                      |

As an alternative to provide the substrates of the present invention the method of thin film coating with a monomer followed by surface curing can be used.

10 The coating formed by the method of the present invention has a thickness of less than 5 microns, and preferably less than 2 microns and most preferably in the range of 0.001 to 1 microns. The coatings are formed by depositing a vapor of curable monomer, under vacuum, on a movable substrate which is mounted in thermal contact with a support, for continuos processing preferably a rotating drum, which is maintained at a temperature below the boiling point of the vaporized monomer under the environmental conditions in vacuum chamber . As a result of this temperature differential, the monomer vapor condenses on the surface of the substrate. The monomer materials utilized in the present invention are relatively low in molecular weight, between 150 and 1000 Atomic Mass Units (AMU) , and preferably in the range 200 to 300 AMU. Polyfunctional fluorocarbons and especially fluoroacrylates or mixtures of monofunctional fluoroacrylates and

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polyfunctional fluoroacrylates are preferred. The monomers or monomer mixtures employed have an average of about two or more double bonds (i.e., a plurality of olefinic groups) and have a vapor pressure such that they condense on the substrate surface. Such vapor pressures are for example pressure between 5 about  $1.33 \cdot 10^{-6}$  mbar and  $1.33 \cdot 10^{-1}$  mbar, most preferably a vapor pressure of approximately  $1.33 \cdot 10^{-2}$  mbar at standard temperature and pressure, (i.e., relatively low boiling materials) are selected.

These high-vapor-pressure monomers can be flash vaporized already at low 10 temperatures and thus are not degraded (cracked) by the heating process. The absence or low amount of unreactive degradation products results in coatings with a reduced levels of volatile components in which substantially all of the deposited monomer is reactive and will cure to form an integral film when exposed to a source of radiation. These properties make it possible to provide a 15 substantially continuous coating despite the fact that the deposited film is very thin. The cured films exhibit excellent adhesion and are resistant to chemical attack by organic solvents and inorganic salts.

The high speed vacuum coating process for producing water vapour permeable 20 substrates with exceptional water repellent properties on either one side or both sides requires a curable monomer component. Desirably, the curable monomer for obtaining water-repellent coatings comprises fluoro-containing group.

In one embodiment, any suitable fluoromonomer may be used, including, but not limited to, fluoroacrylate monomers, fluoro olefin monomers, fluorostyrene 25 monomers, fluoroalkylene oxide monomers (e.g., perfluoropropylene oxide, perfluorocyclohexene oxide), fluorinated vinyl alkyl ether monomers, and the copolymers thereof with suitable comonomers, wherein the comonomers are fluorinated or unfluorinated. Fluoromonomers which are polymerized by a free radical polymerization process are preferred.

30

In one embodiment, fluorostyrenes and fluorinated vinyl alkyl ether monomers which may be used in the method of the present invention include, but are not

limited to,  $\alpha$  -fluorostyrene;  $\beta$  -fluorostyrene;  $\alpha$ ,  $\beta$  -difluorostyrene;  $\beta$ ,  $\beta$  -difluorostyrene;  $\alpha$ ,  $\beta$ ,  $\beta$  -trifluorostyrene;  $\alpha$  -trifluoromethylstyrene; 2,4,6-Tris (trifluoromethyl)styrene; 2,3,4,5,6-pentafluorostyrene; 2,3,4,5,6-pentafluoro-  $\alpha$  -methylstyrene; and 2,3,4,5,6-pentafluoro-  $\beta$  -methylstyrene.

5

In yet another embodiment, tetrafluoroethylene can also be used in the method of the present invention and include, but are not limited to, tetrafluoroethylene-hexafluoropropylene copolymers, tetrafluoroethylene-perfluorovinyl ether copolymers (e.g., copolymers of tetrafluoroethylene with perfluoropropyl vinyl ether), tetrafluoroethylene-ethylene copolymers, and perfluorinated ionomers (e.g., perfluorosulfonate ionomers; perfluorocarboxylate ionomers).

In still another embodiment, fluorocarbon elastomers (see, e.g., 7 Encyclopedia of Polymer Science & Engineering 257) are a group of fluoro olefin polymers which can also be used in the process of the present invention and include, but are not limited to, poly(vinylidene fluoride-co-hexafluoropropylene); poly(vinylidene fluoride-co-hexafluoropropylene-co-tetrafluoroethylene); poly[vinylidene fluoride-co-tetrafluoroethylene-co-perfluoro(methyl vinyl ether)]; poly[tetrafluoroethylene-co-perfluoro(methyl vinyl ether)]; poly(tetrafluoroethylene-co-propylene); and poly(vinylidene fluoride-co-chlorotrifluoroethylene).

In the preferred embodiment, because of their reactivity, physical properties, and the properties of cured films formed from such components, fluoroacrylates are particularly useful monomeric materials. The term "fluoroacrylate monomer," as used herein, refers to esters of acrylic acid ( $\text{H}_2\text{C} = \text{CHCOOH}$ ) or methacrylic acid ( $\text{H}_2\text{C} = \text{CCH}_3 - \text{COOH}$ ), where the esterifying group is a fluorinated group such as perfluoroalkyl. A specific group of fluoroacrylate monomers useful in the method of the invention are compounds represented by formula (I):  $\text{H}_2\text{C} = \text{CR}_1 - \text{COO}(\text{CH}_2)_n\text{R}_2$  (I) wherein: n is 1 or 2;

$R_1$  is hydrogen or methyl; and  $R_2$  is a perfluorinated aliphatic or perfluorinated aromatic group, such as a perfluorinated linear or branched, saturated or unsaturated C<sub>1</sub> to C<sub>10</sub> alkyl, phenyl, or naphthyl.

- 5 In a particular embodiment of the invention,  $R_2$  is a C<sub>1</sub> to C<sub>8</sub> perfluoroalkyl or -CH<sub>2</sub> - NR<sub>3</sub> - SO<sub>2</sub> - R<sub>4</sub>, wherein R<sub>3</sub> is C<sub>1</sub>-C<sub>2</sub> alkyl and R<sub>4</sub> is C<sub>1</sub> to C<sub>8</sub> perfluoroalkyl. The term "perfluorinated," as used herein, means that all or essentially all hydrogen atoms on an organic group are replaced with fluorine. Monomers illustrative of Formula (I) above, and their abbreviations, include the following:
- 10 2-(N-ethylperfluorooctanesulfonamido) ethyl acrylate ("EtFOSEA");  
2-(N-ethylperfluorooctanesulfonamido) ethyl methacrylate ("EtFOSEMA");  
2-(N-methylperfluorooctanesulfonamido) ethyl acrylate ("MeFOSEA");  
2-(N-methylperfluorooctanesulfonamido) ethyl methacrylate ("MeFOSEMA");  
1,1-Dihydroperfluorooctyl acrylate ("FOA"); and
- 15 1,1-Dihydroperfluorooctyl methacrylate ("FOMA").

Alternatively, the curable monomer component can also include polyfunctional acrylates, which are set forth in U.S. Patent 4,842,893.

CLAIMS

1. A surface treated substrate having a fluorocarbon coating characterized in that said treated surface has a static water contact angle (WCA) higher than 5 120°.
2. The substrate of claim 1 characterized in that said treated surface has a static water contact angle (WCA) higher than 130°, preferably between 130° and 165°, most preferably between 155° and 165°.
- 10 3. The substrate of claims 1 or 2 characterized in that said coating is a fluorocarbon coating.
4. The substrate of claim 3 characterized in that said coating exhibits a fluorine/carbon ratio (F/C) of between about 1.50 and about 2.00, preferably between about 1.60 and about 1.95, most preferably substantially equal to 1.75.
- 15 5. The substrate of any preceding claims characterized in that said substrate is selected in the group consisting of polyethylene, polyacrylics, polypropylene, polyvinyl chloride, polyamides, polystyrene, polyurethanes, polyfluorocarbons, polyesters, silicon rubber, hydrocarbon rubbers, polycarbonates, cellulose and its derivatives, rubber, glass, semiconductors, metals, ceramics.
- 20 6. The substrate of any preceding claims characterized in that said substrate is made of a porous material, the porosity of the substrate being substantially unaffected by said coating, preferably said porous material is a perforated film or a fibrous woven or non woven material or an open cell foam material or a porous particulate material.
- 25 7. The substrate of any preceding claims characterized in that said substrate is a flexible substrate.
- 30

8. The substrate of any of the preceding claims characterized in that it is formed into a desired shape prior to being coated.
- 5 9. The substrate of any preceding claims obtainable by exposing the substrate to a modulated plasma glow discharge in the presence of a fluorocarbon gas or vapor.
- 10 10. The substrate of any of the claims 1 to 8, obtainable by coating the substrate with a film of curable monomer and then curing said film

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## CONTINUOUS RF GLOW DISCHARGE

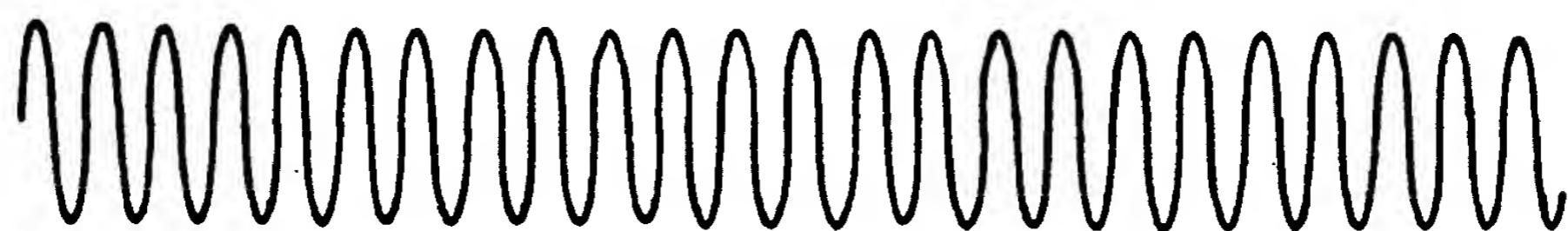


FIG. 1a

## MODULATED RF GLOW DISCHARGE

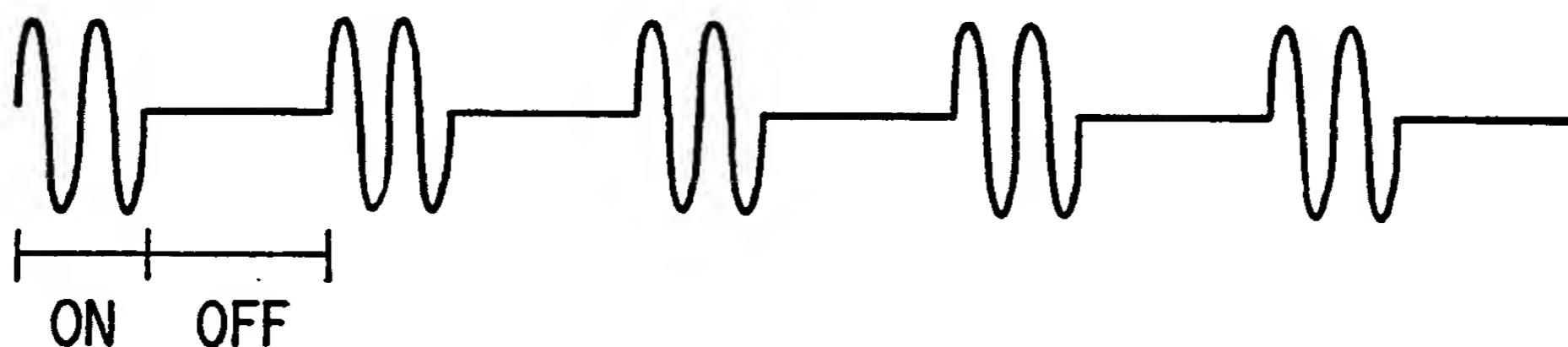


FIG. 1b

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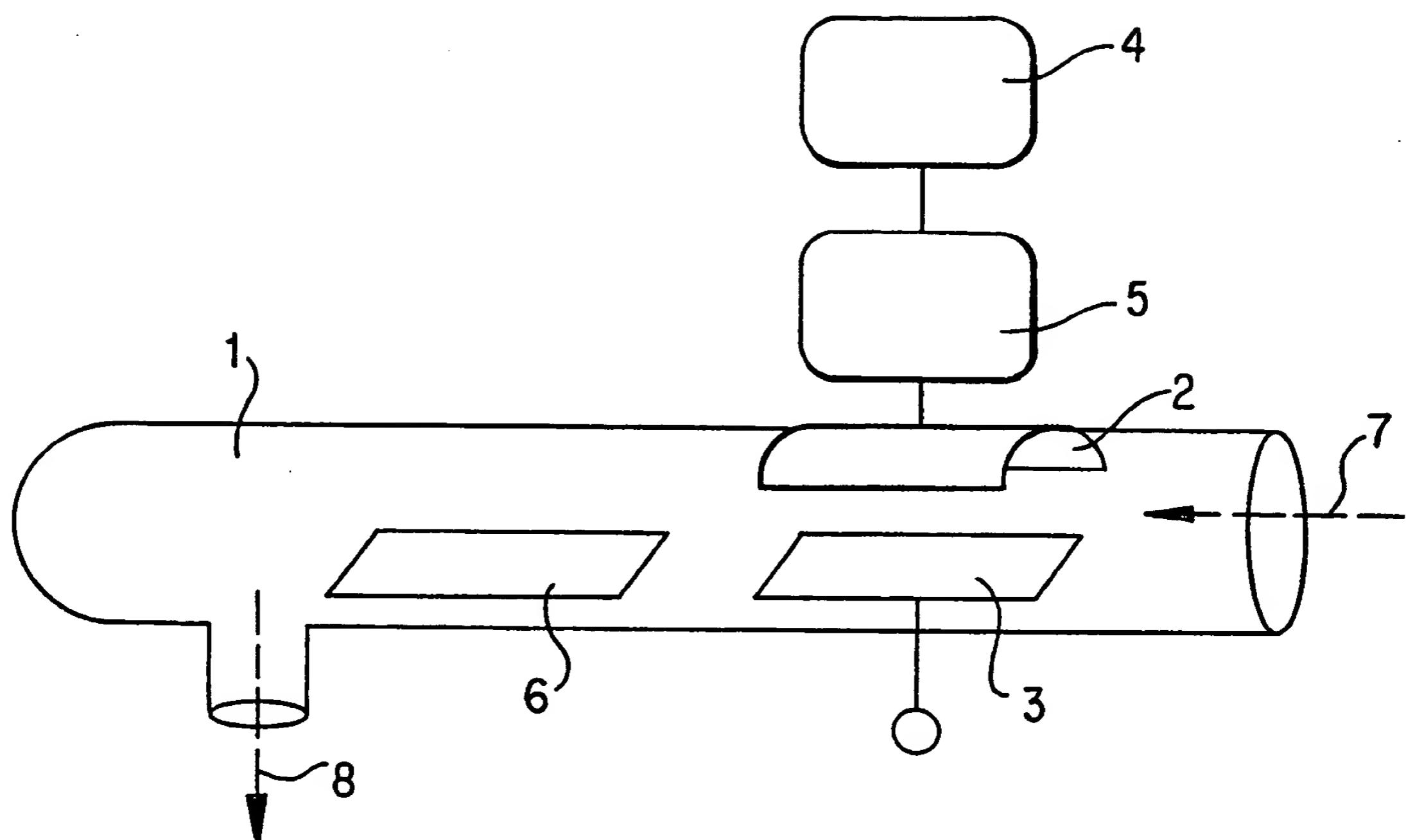


FIG. 2

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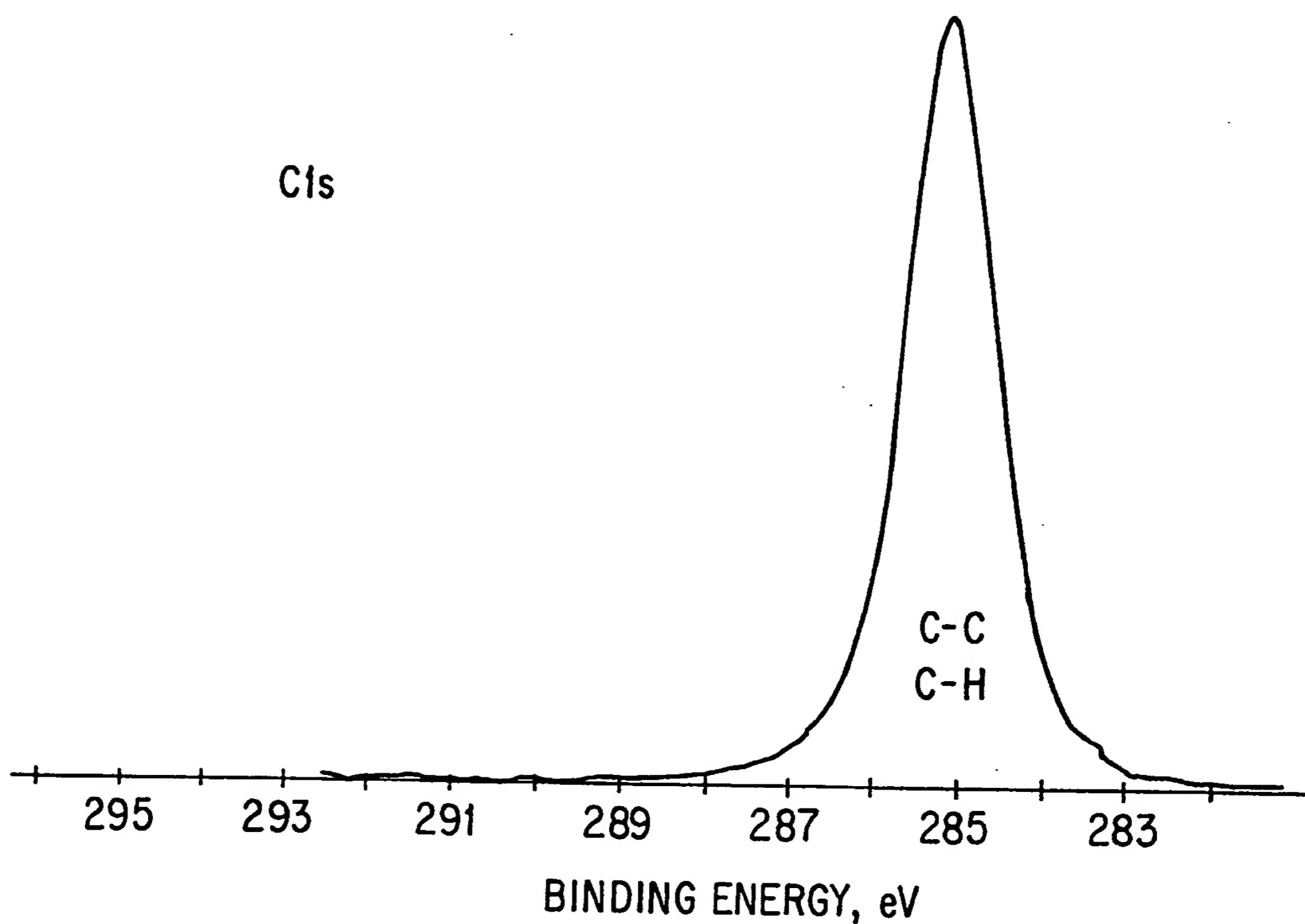


FIG. 3

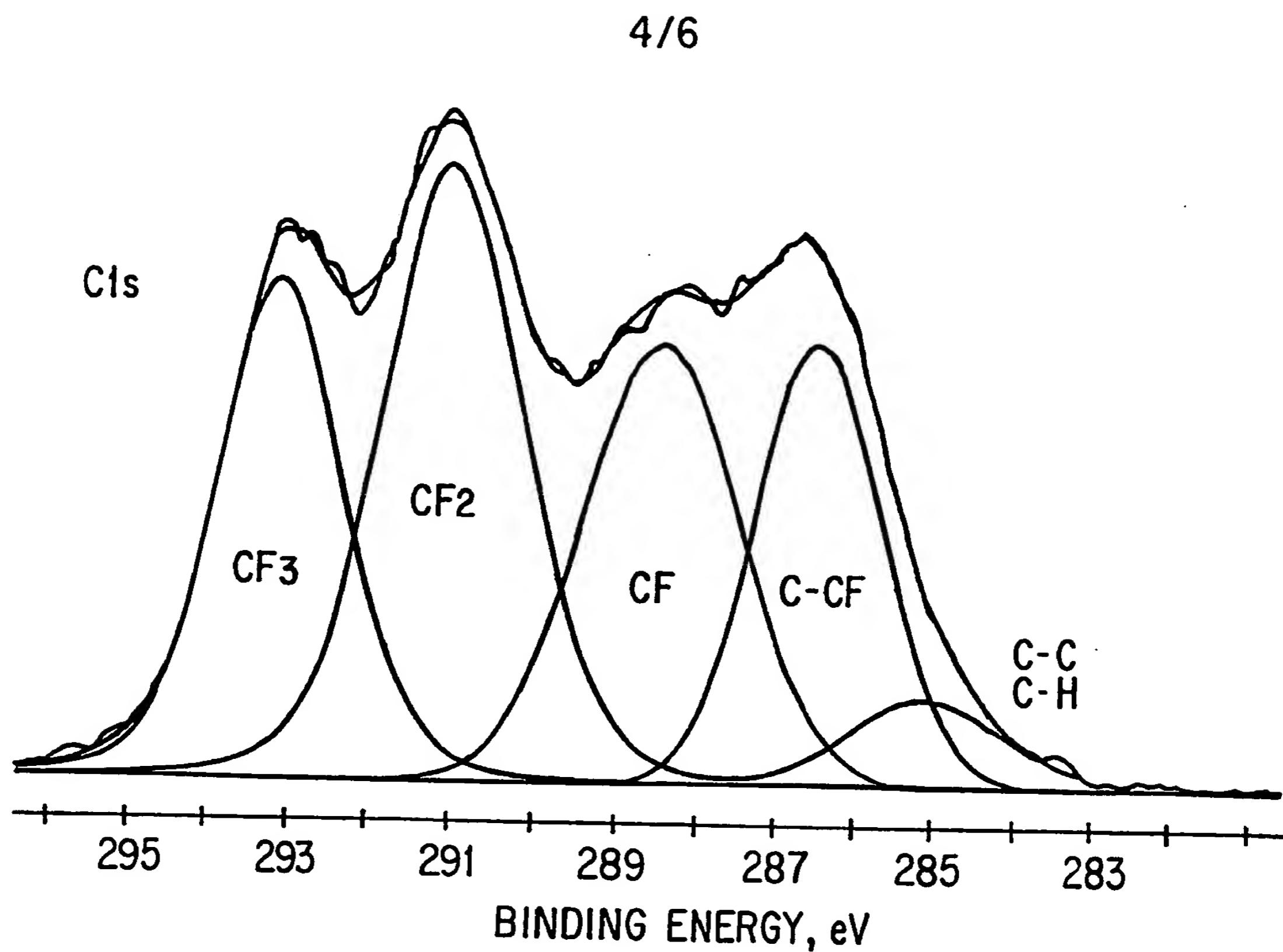


FIG. 4

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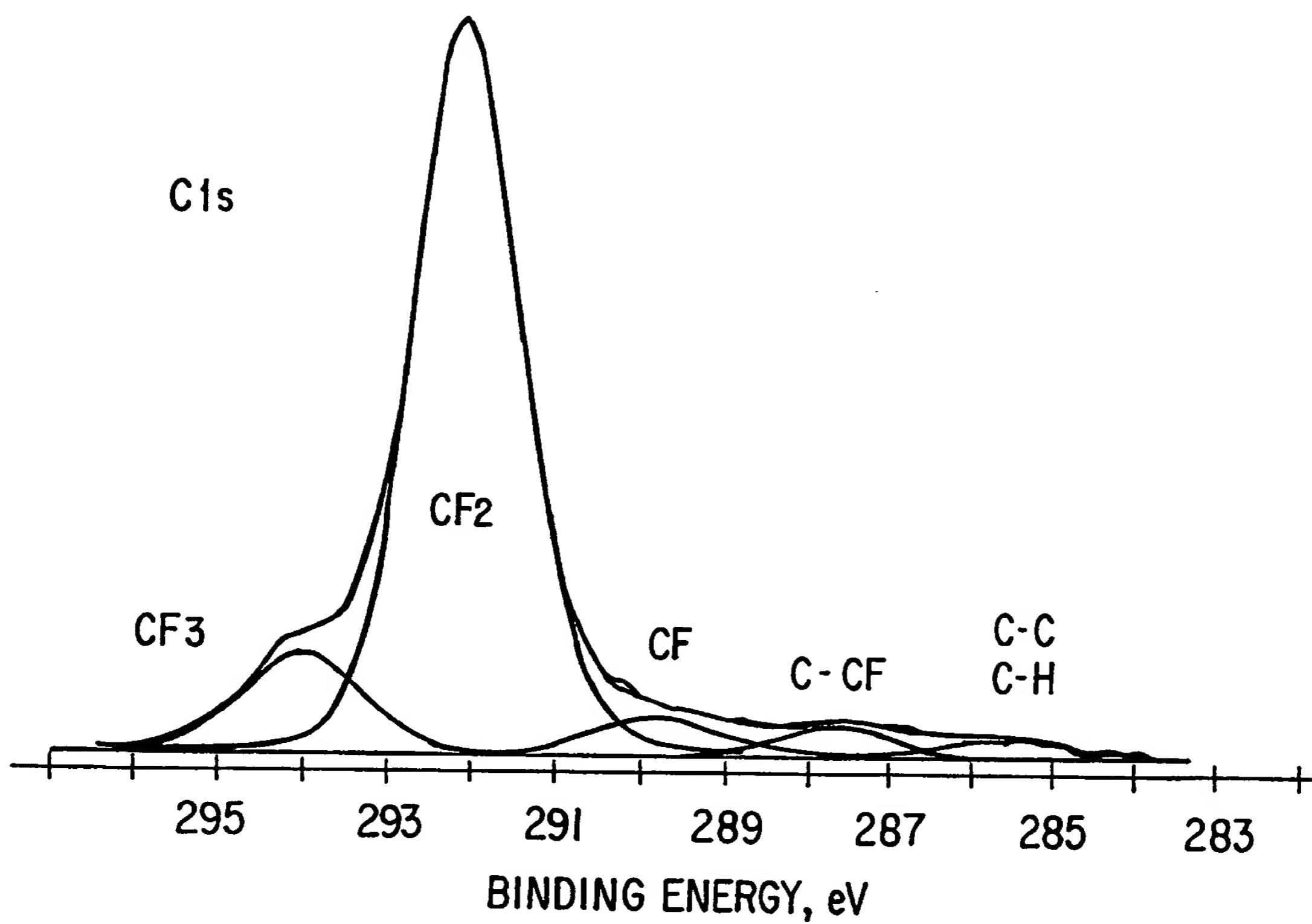


FIG. 5

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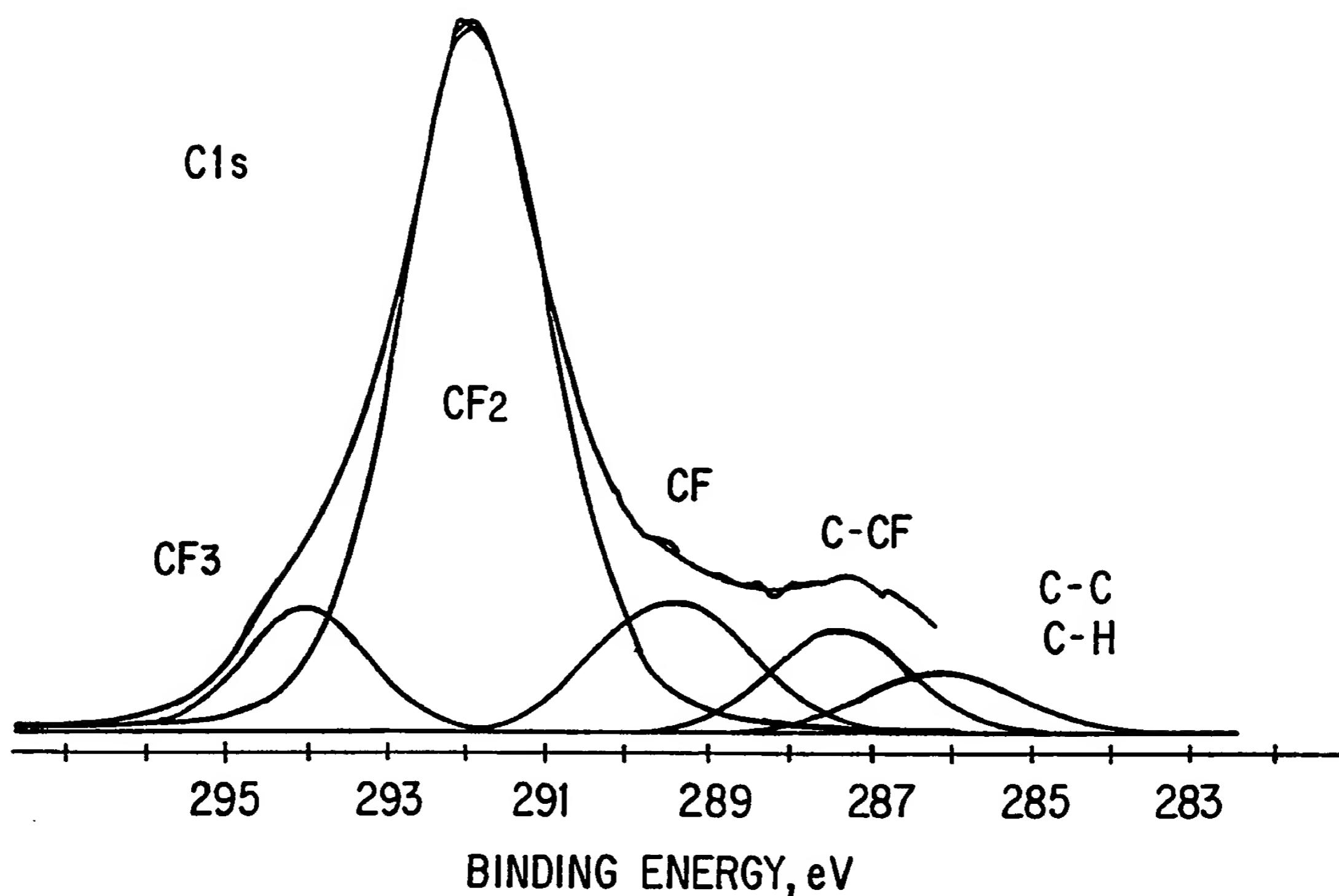


FIG. 6

## INTERNATIONAL SEARCH REPORT

Serial Application No

PCT/US 99/20503

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C16/50 C23C16/30 B05D7/24

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages                                                             | Relevant to claim No. |
|----------|------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X        | US 4 632 842 A (KARWOSKI THEODORE ET AL)<br>30 December 1986 (1986-12-30)<br>column 3, line 3 - line 35<br>column 12, line 1 - line 24<br>---- | 1-7                   |
| X        | EP 0 531 029 A (GEN ELECTRIC)<br>10 March 1993 (1993-03-10)<br>column 4, line 6 - line 31; claims 9-13<br>----                                 | 1,3,5                 |
| A        | WO 97 42356 A (MASSACHUSETTS INST<br>TECHNOLOGY) 13 November 1997 (1997-11-13)<br>page 9, line 3 -page 15, line 2; claims<br>16,20,24<br>----- | 8-10                  |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

Information on patent family members

National Application No

PCT/US 99/20503

| Patent document cited in search report |   | Publication date | Patent family member(s) |           | Publication date |
|----------------------------------------|---|------------------|-------------------------|-----------|------------------|
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|                                        |   |                  | ZA                      | 9206153 A | 29-05-1993       |
| WO 9742356                             | A | 13-11-1997       | US                      | 5888591 A | 30-03-1999       |
|                                        |   |                  | EP                      | 0920542 A | 09-06-1999       |